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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.058
wR factor = 0.143
Data-to-parameter ratio = 8.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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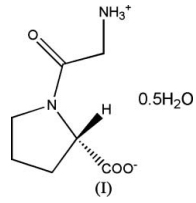
The crystal structure of glycyl-L-proline (GLY–PRO) hemihydrate, $C_7H_{12}N_2O_3{\cdot}0.5H_2O$, has two molecules of GLY–PRO in the asymmetric unit; one molecule adopts the *cis* configuration at the peptide bond and the other adopts the *trans* configuration.

Comment

The *trans* form of the peptide bond is generally favoured over the *cis* form by a ratio of around 1000 to 1 (*ca* 7.5 kJ mol^{-1} at 300 K) as the result of more favourable steric interactions between side chains (Glusker *et al.*, 1994). In the case of proline, however, this ratio drops to 4 to 1 (see, for example, Creighton, 1993).



(I)

Glycyl-L-proline (GLY–PRO), a dipeptide consisting of a glycine (GLY) residue at the N-terminus and a proline (PRO) residue at the carboxy terminus, provides an excellent example of a simple structure relevant to protein folding. *cis*–*trans* Isomerization of the prolyl peptide bond has been implicated in the slow refolding of proteins (*e.g.* Brandts *et al.*, 1975) and nature has overcome this potential restriction by providing a prolyl isomerase.

Recrystallization of GLY–PRO by slow diffusion of ethanol into an aqueous solution yielded crystals of the hemihydrate, (I). The structure of (I) contains two GLY–PRO molecules in the asymmetric unit, *viz.* one (based on N11) in the *trans* form and the other in the *cis* form (Figs. 1 and 2, respectively). The relevant ω torsion angles are, in the *trans* form, τ(C21—C31—N51—C91) = −174.3 (4)° and, in the *cis* form, τ(C22—C32—N52—C92) = −3.3 (7)°.

The two molecules interact with each other *via* hydrogen bonds between the carboxylate and ammonium groups. The water molecules are double hydrogen-bond donors, linking *cis* to *trans* isomers *via* their carboxylate groups. Overall, the hydrogen bonds form double layers which stack along the *a* direction (Figs. 3 and 4).

Experimental

A sample of glycyl-L-proline was obtained from Sigma–Aldrich. Crystals were grown at room temperature by slow diffusion of

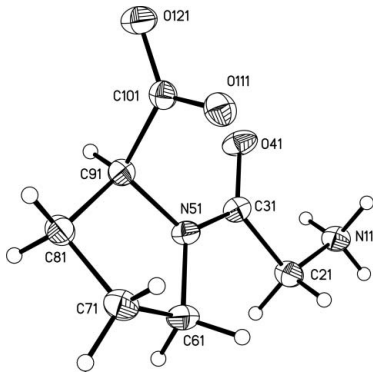


Figure 1
The structure of GLY–PRO in (I) in its *trans* configuration. The ellipsoids enclose 30% probability surfaces.

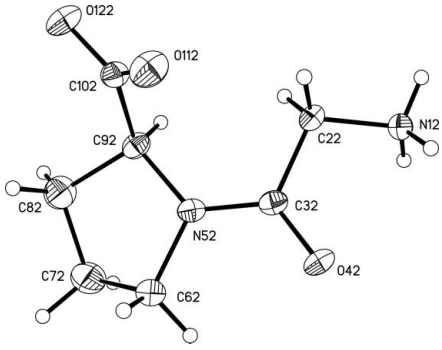


Figure 2
Structure of GLY–PRO in (I) in its *cis* configuration. The ellipsoids enclose 30% probability surfaces.

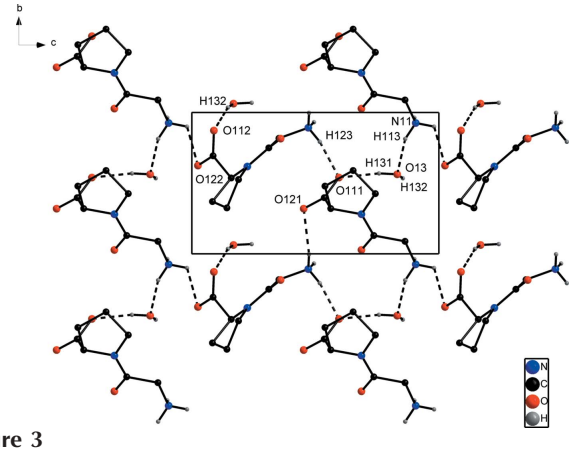


Figure 3
Hydrogen bonding (dashed lines) in layers formed in the structure of (I), viewed along [100].

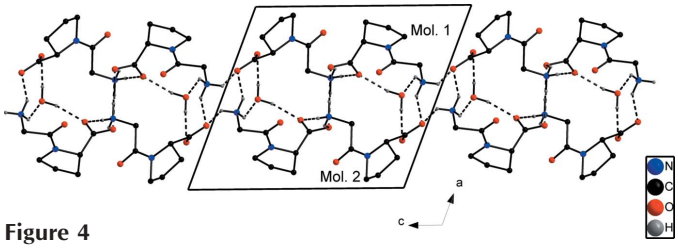


Figure 4
Pairs of layers depicted in Fig. 3 are connected though further hydrogen bonds (dashed lines). The double layers so formed stack along the *a* direction. This view is along [010]; Mol. 1 and Mol. 2 contain atoms N11, C21 *etc*. and N12, C22 *etc*., respectively.

ethanol into an aqueous solution over a period of 7 d. Data were collected at room temperature, rather than low temperature, as a preliminary to a high-pressure study, which was also to have been carried out at room temperature. In the event, the crystals proved too weakly diffracting for the high-pressure study.

Crystal data

$C_7H_{12}N_2O_3{\cdot}0.5H_2O$
M_r = 181.19
Monoclinic, $P2_1$
a = 11.171 (4) Å
b = 6.619 (3) Å
c = 12.371 (5) Å
β = 110.818 (7)°
V = 855.0 (6) Å^3
Z = 4
D_x = 1.408 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 685 reflections
θ = 4–20°
μ = 0.11 mm^{-1}
T = 293 K
Block, colourless
0.12 × 0.11 × 0.09 mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)
T_{min} = 0.73, T_{max} = 0.99
5465 measured reflections
1909 independent reflections
1487 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 26.4°
$h = -13 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.143
S = 0.98
1908 reflections
233 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.49P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C21	1.467 (6)	N12—C22	1.461 (5)
C21—C31	1.526 (6)	C22—C32	1.515 (6)
C31—O41	1.219 (5)	C32—O42	1.217 (5)
C31—N51	1.332 (5)	C32—N52	1.334 (5)
N51—C61	1.474 (5)	N52—C62	1.470 (6)
N51—C91	1.471 (5)	N52—C92	1.467 (5)
C61—C71	1.511 (7)	C62—C72	1.503 (9)
C71—C81	1.515 (7)	C72—C82	1.521 (7)
C81—C91	1.538 (6)	C82—C92	1.549 (7)
C91—C101	1.529 (6)	C92—C102	1.524 (6)
C101—O111	1.253 (6)	C102—O112	1.231 (6)
C101—O121	1.253 (5)	C102—O122	1.268 (5)
N11—C21—C31	108.8 (4)	N12—C22—C32	110.3 (3)
C21—C31—O41	120.8 (4)	C22—C32—O42	119.3 (4)
C21—C31—N51	115.6 (4)	C22—C32—N52	117.4 (4)
O41—C31—N51	123.6 (4)	O42—C32—N52	123.3 (4)
C31—N51—C61	127.3 (3)	C32—N52—C62	120.8 (4)
C31—N51—C91	119.9 (3)	C32—N52—C92	127.0 (3)
C61—N51—C91	112.8 (3)	C62—N52—C92	112.1 (4)
N51—C61—C71	103.3 (3)	N52—C62—C72	102.3 (4)
C61—C71—C81	104.0 (4)	C62—C72—C82	104.2 (4)
C71—C81—C91	104.5 (4)	C72—C82—C92	104.3 (4)
C81—C91—N51	102.1 (3)	C82—C92—N52	103.5 (3)
C81—C91—C101	112.9 (3)	C82—C92—C102	111.4 (4)
N51—C91—C101	111.3 (3)	N52—C92—C102	113.9 (4)
C91—C101—O111	118.3 (4)	C92—C102—O112	120.6 (4)
C91—C101—O121	117.9 (4)	C92—C102—O122	114.8 (4)
O111—C101—O121	123.7 (4)	O112—C102—O122	124.6 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H112···O122^{i}	0.90	1.95	2.728 (5)	143
N11—H113···O13^{ii}	0.90	2.11	2.789 (6)	131
N12—H121···O121^{iii}	0.90	2.11	2.876 (5)	142
N12—H122···O121^{iv}	0.90	2.15	2.896 (6)	140
N12—H123···O111	0.90	1.95	2.839 (5)	168
O13—H131···O111	0.85 (1)	1.91 (2)	2.739 (5)	164 (5)
O13—H132···O112^{i}	0.85 (1)	2.06 (3)	2.872 (5)	160 (6)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+1$; (ii) $x, y-1, z$; (iii) $-x+1, y+\frac{1}{2}, -z+1$; (iv) $x, y+1, z$.

H atoms in the GLY–PRO molecules were all placed in calculated positions, with U_{iso}(H) = 1.2U_{eq}(C,N), C—H = 0.99 and 1.00 Å, and N—H = 0.90 Å. The H atoms of the water of crystallization (O13) were located in a difference map and refined, subject to the restraints O—H = 0.85 (1) Å and H—O—H = 105 (1)°. A common isotropic displacement parameter was also refined. The 102 reflection was omitted from the refinement since it seemed to suffer from the effects of extinction. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged. The absolute configuration of the model reported here is based on the known configuration of the sample.

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *XP* (Sheldrick, 1997) and *DIAMOND* (Crystal Impact, 2004); software used to prepare material for publication: *CRYSTALS*.

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